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⑤④ **Apparatus for cleaning an optical element for use with a radiation beam.**

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**WO-A-87/02603**  
**US-A- 4 555 303**  
**PATENT ABSTRACTS OF JAPAN, vol. 9, no. 283 (C-313)[2006], 9th November 1985 ; & JP-A-60 129 136**  
**PATENT ABSTRACTS OF JAPAN, vol. 9, no. 125 (C-283)[1848], 30th May 1985 ; & JP-A-60 12 128**  
**APPLIED OPTICS, vol. 26, no. 18, 15th September 1987, pp. 3884-3894 ; T. KOIDE et al.: "Resuscitation of carbon-contaminated mirrors and gratings by oxygen-discharge cleaning. 1 : Efficiency recovery in the 4-40-eV range"**

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## Description

### FIELD OF THE INVENTION AND RELATED ART

This invention relates to an apparatus for removing impurities deposited on an optical element for use with a radiation beam such as a synchrotron orbit radiation beam, for example.

If an optical element is used with a radiation beam for a long period, carbon (C), for example, is deposited onto such portion of the surface of the optical element having been irradiated with the radiation beam. This raises a problem of deterioration of the property of the optical element. In the past, experiments were made to remove deposited carbon by using oxygen plasma ("Applied Optics", Vol. 26, No. 18/15, September, 1987).

However, because of use of the oxygen plasma, the proposed method of removing impurities involves the following inconveniences. That is, like the addition of electrode means for producing plasma, it needs modification of a chamber or provision of other additional devices. Also, since the optical element as a whole is exposed to the plasma, there is a possibility that a non-contaminated portion is damaged.

Furthermore, JP-A-60-12128 discloses a photochemical surface treating apparatus comprising a chamber for receiving an object to be treated, means for evacuating the chamber, means for introducing gas, and a lamp for irradiating the object at a desired wavelength; and JP-A-60-129136 discloses an irradiating apparatus comprising a chamber for receiving an object to be treated, means for evacuating polluted gases, means for introducing oxygen to said chamber, and an ultraviolet lamp for irradiating the object.

### SUMMARY OF THE INVENTION

The present invention is defined in claim 1. An object thereof is an apparatus for removing impurities deposited on an optical element with a simple process by which the optical element is less damaged. This object can be achieved by removing impurities from the surface of the optical element by means of photochemical etching.

The device structure for the photochemical etching is quite simple, and only the addition of a gas discharging system to an optical element chamber as well as a gas inlet port and a light transmitting filter at the radiation beam input side, is necessary.

The mechanism of reaction is such that: in an occasion where oxygen, for example, is used as a reactive gas, light of a wavelength shorter than 2537 angstroms is projected to the oxygen, by which ozone is produced. This absorbs light shorter than 8500 angstroms, by which molecule oxygen and atom oxygen are produced. Since the atom oxygen is active, it reacts with carbon which is the component of the un-

clear matter on the surface of the optical element, to gasify it. The resultant gas is then discharged.

With this mechanism, no physical force is applied to the surface of the optical element and, therefore, there is no possibility of damage of the element.

These and other objects, features and advantages of the present invention will become more apparent upon a consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the accompanying drawing.

### BRIEF DESCRIPTION OF THE DRAWING

The accompanying drawing is a schematic representation, showing the basic structure of a cleaning device of the present invention when it is used in an exposure system.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

#### Embodiment 1 :

In this embodiment, in the basic structure of the present invention as illustrated in the drawing, as an optical element 7 for use with a radiation beam, a grazing incidence mirror made of silicon dioxide ( $\text{SiO}_2$ ) coated with gold (Au) is used.

Radiation beam emitted by an electron accumulation ring 1 is projected to the grazing incidence mirror 7 through a beam line 2. For this projection, the inside of a chamber 6 in which the mirror 7 is placed is evacuated through an evacuation line 8 and the inside vacuum is maintained not greater than  $10^{-8}$  Torr, for example, about  $5 \times 10^{-9}$  Torr.

If the radiation beam from the electron accumulation ring 1 is projected continuously to the mirror 7 for a long time period, impurity mainly consisting of carbon (C) is deposited to the reflection surface of the mirror 7. According to simulated measurement of the reflectivity, assuming that the mirror is irradiated with the radiation beam for about one year, the mirror surface reflectivity decreases, on the average, to about 70 - 80 % of its original reflectivity. Particularly, in the wavelength range near 44 angstroms which corresponds to the wavelength at the absorption edge of the carbon, the reflectivity decreases to about 30 %. To such reflectivity-decreased mirror 7, the surface cleaning of the present invention may be conducted, by which the original reflectivity can be restored. This will be explained below in greater detail.

First, a protection valve 3 and a transmission filter 4 provided along the beam line 2 are closed by using a linear motion coupler, and the transmission filter 4 is positioned in the beam line 2. Then, a valve 9 which is provided at a side of the mirror chamber 6 facing to an exposure apparatus 11, is closed and,

thereafter, an oxygen gas is introduced into the mirror chamber 6 through a gas inlet 5. The protection valve 3 is provided to avoid breakage of the filter 4 due to a differential pressure to be produced between the beam line 2 and the mirror chamber 6 as the oxygen gas is introduced from the gas inlet 5, which breakage has a considerable effect on the electron accumulation ring (synchrotron) 1 as a whole. Thus, essentially it may be omitted. However, in consideration of safety, use of the protection valve is desirable.

Also, in order to prevent a possibility that a large force is applied at a moment to the transmission filter 4 as the oxygen gas is introduced, it is desirable to provide a needle valve 20 or the like at the gas inlet 5 such that the gas is introduced slowly. The evacuation line 8 is coupled to a vacuum source (not shown), and a conductance valve 21 or the like effective to reduce the conductance is disposed at an end portion of the evacuation line 8, to allow slow leakage. Under such slow leakage, the inside pressure of the mirror chamber 6 is maintained at a few torrs, for example, about 2 torrs. After this, the protection valve 3 is opened, whereby the radiation beam from the electron accumulation ring 1 is projected to the transmission filter 4. Thus, the light transmitted through this filter 4 is projected to the reflection surface of the mirror 7. Here, the transmission filter 4 may be made of silica ( $\text{SiO}_2$ ) of a thickness of 0.5 mm. In that occasion, light containing a wavelength component of 2537 angstroms and having an energy sufficient for accelerating the reaction of oxygen introduced into the mirror chamber 6 with carbon deposited to the reflection surface of the mirror 7, can be supplied from the filter 4 to the mirror 7.

Leaving this condition for about fifteen (15) hours, the cleaning process may be completed. According to simulated measurement, the reflectivity of the mirror 7 can be restored to a level not lower than 95 % of its original reflectivity.

The exposure apparatus 11 in this example is used to print a pattern of a mask 15 on a semiconductor wafer 16 in a step-and-repeat manner, by using the radiation beam (X-rays) emanating from the electron accumulation ring 1 and reflected by the mirror 7. In the attached drawing, denoted at 12 is a beryllium film (beryllium window) for isolating a high vacuum at the mirror chamber 6 side from a reduced-pressure helium gas ambience at the exposure apparatus 11 side, in the operation of the exposure apparatus 11. Denoted at 13 is a shutter for controlling the exposure (the amount of exposure) of the mask 15 and the wafer 16 with the radiation beam from the mirror 7. Denoted at 14 is a mask holder for holding the mask 15 at the illustrated exposure position. Denoted at 17 is a wafer stage for holding the wafer 16 and being movable in the y-axis (vertical) and x-axis (horizontal) directions, for step-and-repeat exposures of the wafer 16. These components are accommodated in an ex-

posure chamber 30, and they are surrounded by the reduced-pressure helium gas ambience.

#### Embodiment 2 :

In this embodiment, in the basic structure of the present invention illustrated in the attached drawing, as an optical element 7 for use with a radiation beam, a diffraction grating (twelve hundred lines per millimeter) made of silica ( $\text{SiO}_2$ ) is used.

Radiation beam emitted by the electron accumulation ring 1 is projected to the diffraction grating 7 through the beam line 2. In this projection, the inside of a chamber 6 in which the diffraction grating is accommodated, is maintained at a vacuum of not greater than  $10^{-8}$  Torr for example,  $5 \times 10^{-9}$  Torr.

According to simulation, if the radiation beam is projected to the diffraction grating for about seven months, the intensity of first-order diffraction light of the light inputted to the diffraction grating at an angle of 20 degrees with respect to a normal to the diffraction grating, decreases to about 10 % of that as attainable before irradiation with the radiation beam.

To such diffraction grating, a similar cleaning process as Embodiment 1 may be conducted. In this embodiment, the transmission filter may be made of silica ( $\text{SiO}_2$ ) of a thickness of 1 mm, while the oxygen gas pressure may be at 5 Torr. According to simulation, by projecting the filter-transmitted light to the surface of the diffraction grating for twelve (12) hours, the diffraction efficiency can be restored to a level of 90 % of the original efficiency.

#### Embodiment 3 :

In this embodiment, as an optical element for use with a radiation beam, a grazing incidence mirror made of silica ( $\text{SiO}_2$ ) and coated with gold, is used.

The grazing incidence mirror 7 is disposed in a chamber 6 the inside of which is maintained at a pressure not greater than  $10^{-8}$  Torr, for example, about  $5 \times 10^{-9}$  Torr. According to simulated measurement of reflectivity, if the mirror surface is irradiated with the radiation beam from the electron accumulation ring 1 for about one year, the reflectivity decreases, on the average, to about 80 % of the original reflectivity. In this embodiment, by using a heater (not shown), such reflectivity-reduced mirror 7 is heated so that its surface temperature rises to 200 °C, and then the cleaning process is conducted in a similar manner as in Embodiment 1. In the present embodiment, the oxygen pressure in the chamber 6 may be held at a few torrs, for example, 2 torrs. Also, the transmission filter 4 may be made of silicon nitride ( $\text{Si}_3\text{N}_4$ ) of a thickness of 0.2 micron formed by back-etching.

Leaving this condition for twelve hours, the cleaning process may be completed. According to simulation, the reflectivity can be restored to a level not low-

er than 95 % (average) of the original reflectivity.

#### Embodiment 4 :

In this embodiment, as an optical element for use with a radiation beam, a grazing incidence mirror made of silica ( $\text{SiO}_2$ ) coated with platinum (Pt) is used.

The grazing incidence mirror 7 is disposed in a chamber 6 the inside of which is maintained at a pressure not greater than  $10^{-8}$  Torr, for example, about  $5 \times 10^{-9}$  Torr. According to simulated measurement of reflectivity, if the grazing incidence mirror is irradiated with the radiation beam from the electron accumulation ring 1 for about one year, the reflectivity decreases on the average to about 75 % of the original reflectivity of the mirror. To such reflectivity-decreased mirror, a cleaning process of the present invention may be conducted. In this embodiment, the pressure in the chamber 6 may be a few torrs, for example, 2 torrs. Also, the transmission filter may be provided by a silica plate of a thickness 1 mm. In this embodiment, ozone prepared separately is introduced into the chamber 6, and the cleaning process is carried out.

Leaving this condition for twelve hours, the cleaning process may be completed. According to simulated measurement of the reflectivity, the reflectivity can be restored, on the average, to 95 % or more of the original reflectivity.

As described hereinbefore, with the method and apparatus for cleaning an optical element for use with a radiation beam, it is possible to remove carbon deposited on the optical element, which leads to deterioration of the performance of the optical element, with a simple structure and without damaging the optical element. Thus, it is possible to restore the property of the optical element.

Further, in accordance with the present invention, the cleaning process for removing carbon or the like can be executed within a vacuum ambience, and, thus, without exposure to atmosphere. Also, the cleaning process can be executed without demounting the optical element. Thus, it is possible to reduce the time necessary for demounting/mounting and for aligning the optical element. Further, the device structure as well as added components are simple. Also, there is no possibility of damaging the surface (coating) of the optical element. Consequently, the present invention is significantly contributable to easy maintenance of an optical element to be used with a radiation beam, to which attention has not been paid. This ensures effective utilization of the synchrotron radiation beam in terms of function and also of time.

#### Claims

1. Apparatus for irradiating a substrate, said apparatus comprising a source (1) providing a beam of electromagnetic radiation, a vacuum chamber (6), means (8, 21) for evacuating said chamber and an optical element (7) mounted in said chamber (6) in order to receive said beam and to direct it towards the location of said substrate; said apparatus being characterised by:  
gas supplying means (5, 20) for supplying into said chamber (6) a gas able to react photochemically with impurities deposited on the surface of said optical element (7) and selecting means (4) for selecting radiation of a desired wavelength range from said source (1), whereby, upon introduction of said gas in said chamber (6) and actuation of said source (1) and said selecting means (4), the beam receiving surface portion of said optical element (7) can be cleaned via photochemical etching from impurities deposited thereon without demounting said optical element (7).
2. An apparatus as claimed in claim 1, wherein said optical element (7) comprises a reflector.
3. An apparatus as claimed in claim 1 or 2, characterised in that said gas supplying means (5, 20) are arranged to supply oxygen gas.
4. An apparatus as claimed in claim 1 or 2, characterised in that said gas supplying means (5, 20) are arranged to supply ozone gas.
5. An apparatus as claimed in claim 2, wherein supporting means (11) are provided for supporting a wafer substrate (16) for exposure to said radiation beam reflected by said optical element (7).
6. An apparatus as claimed in claim 5, wherein said supporting means (11) is provided with a mask (15), whereby on exposure of said wafer (16) by said beam, a pattern of said mask is transferred onto the wafer.
7. An apparatus as claimed in claim 5, characterised in that means are provided to actuate said gas supplying means (5, 20), said source (1) and said selecting means (4) to remove impurities from said surface portion of said optical element (7) during a time period in which exposure of said wafer (16) is not operated.
8. An apparatus as claimed in any one of claims 1-7, characterised in that said selecting means (4) comprises a filter (4) provided between said source (1) and said chamber (6) for selecting the

desired wavelength range from the beam.

9. An apparatus as claimed in claim 8, characterised in that said filter (4) is made of silica.
10. An apparatus as claimed in claim 1, wherein said source (1) comprises a synchrotron radiation source.

#### Patentansprüche

1. Vorrichtung zum Bestrahlen eines Substrats, wobei die Vorrichtung eine Quelle (1), die ein Bündel aus elektromagnetischer Strahlung zur Verfügung stellt, eine Vakuumkammer (6), Einrichtungen (8, 21) zum Evakuieren der Kammer und ein optisches Element (7), das in der Kammer (6) angebracht ist, um den Strahl zu empfangen und ihn zu der Stelle des Substrats zu richten, umfaßt; wobei die Vorrichtung gekennzeichnet ist durch :  
Gaszufuhreinrichtungen (5, 20) zum Zuführen eines Gases mit der Fähigkeit, photochemisch mit auf der Oberfläche des optischen Elements (7) abgeschiedenen Verunreinigungen zu reagieren, in die Kammer (6) und Auswahleinrichtungen (4) zum Auswählen von Strahlung eines erwünschten Wellenlängenbereichs von der Quelle (1), wodurch, bei Einführen des Gases in die Kammer (6) und Betätigung der Quelle (1) und der Auswahleinrichtung (4) der strahlaufnehmende Oberflächenbereich des optischen Elements (7) durch photochemisches Ätzen von auf dem optischen Element abgeschiedenen Verunreinigungen gereinigt werden kann, ohne das optische Element (7) zu demontieren.
2. Vorrichtung nach Anspruch 1, wobei das optische Element (7) einen Reflektor umfaßt.
3. Vorrichtung nach einem der Ansprüche 1 und 2, dadurch gekennzeichnet, daß die Gaszufuhreinrichtungen (5, 20) zur Zufuhr von Sauerstoffgas angeordnet sind.
4. Vorrichtung nach einem der Ansprüche 1 und 2, dadurch gekennzeichnet, daß die Gaszufuhreinrichtungen (5, 20) zur Zufuhr von Ozongas angeordnet sind.
5. Vorrichtung nach Anspruch 2, wobei Halteeinrichtungen (11) zum Halten eines Wafersubstrats (16) zur Belichtung mit dem von dem optischen Element (7) reflektierten Strahlungsbündel bereitgestellt sind.
6. Vorrichtung nach Anspruch 5, wobei die Halteein-

richtung (11) mit einer Maske ausgestattet ist, wodurch bei Belichtung des Wafers (16) mit dem Strahl ein Muster der Maske auf den Wafer übertragen wird.

7. Vorrichtung nach Anspruch 5, dadurch gekennzeichnet, daß Einrichtungen bereitgestellt sind, um die Gas-Zufuhreinrichtungen (5, 20), die Quelle (1) und die Auswahleinrichtungen (4) zu betätigen, um Verunreinigungen von dem Oberflächenbereich des optischen Elements (7) während einer Zeitdauer, in der die Belichtung des Wafers (16) nicht durchgeführt wird, zu entfernen.
8. Vorrichtung nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß die Auswahleinrichtung (4) einen Filter (4), der zwischen der Quelle (1) und der Kammer (6) zum Auswählen des erwünschten Wellenlängenbereichs von dem Strahl bereitgestellt ist, umfaßt.
9. Vorrichtung nach Anspruch 8, dadurch gekennzeichnet, daß der Filter (4) aus Siliziumdioxid gemacht ist.
10. Vorrichtung nach Anspruch 1, wobei die Quelle (1) eine Synchrotron-Strahlungsquelle umfaßt.

#### Revendications

1. Appareil pour irradier un substrat, cet appareil comprenant une source (1) qui produit un faisceau de rayonnement électromagnétique, une chambre à vide (6), des moyens (8, 21) pour faire le vide dans la chambre et un élément optique (7) monté dans la chambre (6) de façon à recevoir le faisceau et à le diriger vers l'emplacement du substrat ; cet appareil étant caractérisé par :  
des moyens d'alimentation en gaz (5, 20) destinés à introduire dans la chambre (6) un gaz capable de réagir de façon photochimique avec des impuretés déposées sur la surface de l'élément optique (7), et des moyens de sélection (4) pour sélectionner le rayonnement par la source (1) d'une gamme de longueurs d'onde désirée, grâce à quoi, sous l'effet de l'introduction du gaz dans la chambre (6) et de l'actionnement de la source (1) et des moyens de sélection (4), la partie de la surface de l'élément optique (7) qui reçoit le faisceau peut être nettoyée par attaque photochimique, de façon à être débarrassée d'impuretés déposées sur elle, sans démonter l'élément optique (7).
2. Un appareil selon la revendication 1, dans lequel l'élément optique (7) comprend un réflecteur.

3. Un appareil selon la revendication 1 ou 2, caractérisé en ce que les moyens d'alimentation en gaz (5, 20) sont conçus pour fournir de l'oxygène.
4. Un appareil selon la revendication 1 ou 2, caractérisé en ce que les moyens d'alimentation en gaz (5, 20) sont conçus pour fournir de l'ozone. 5
5. Un appareil selon la revendication 2, dans lequel des moyens de support (11) sont prévus pour supporter un substrat (16) consistant en une tranche, pour l'exposition au faisceau de rayonnement qui est réfléchi par l'élément optique (7). 10
6. Un appareil selon la revendication 5, dans lequel les moyens de support (11) sont munis d'un masque (15), grâce à quoi sous l'effet de l'exposition de la tranche (16) par le faisceau, un motif de ce masque est transféré sur la tranche. 15
7. Un appareil selon la revendication 5, caractérisé en ce que des moyens sont prévus pour actionner les moyens d'alimentation en gaz (5, 20), la source (1) et les moyens de sélection (4), de façon à éliminer des impuretés de la partie de surface de l'élément optique (7) pendant un intervalle de temps au cours duquel l'exposition de la tranche (16) n'a pas lieu. 20 25
8. Un appareil selon l'une quelconque des revendications 1-7, caractérisé en ce que les moyens de sélection (4) comprennent un filtre (4) qui est placé entre la source (1) et la chambre (6), pour sélectionner à partir du faisceau la gamme de longueurs d'onde désirée. 30 35
9. Un appareil selon la revendication 8, caractérisé en ce que le filtre (4) est en silice.
10. Un appareil selon la revendication 1, dans lequel la source (1) consiste en une source de rayonnement synchrotron. 40

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